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(54) Title: CATALYTIC CONVERTER FOR A LEAN BURN INTERNAL COMBUSTION ENGINE

(57) Abstract

A layered exhaust gas catalyst containing Pt in a first layer and Rh in a second layer is more selective for catalysing the reaction between NOx and/or nitrate with hydrocarbons and/or CO than for catalysing the reaction between hydrocarbons and/or CO with oxygen. NOx can be reduced to N_2 under constant lean to stoichiometric conditions without the need for rich spikes.

CATALYTIC CONVERTER FOR A LEAN BURN INTERNAL COMBUSTION ENGINE

The present invention concerns improvements in emissions control, especially in the control of NOx under lean conditions.

The problems of controlling regulated emissions from internal combustion engines are well known. A particular difficulty is the reduction of NOx to in the case of "lean-burn" motors of various types, because there is generally an excess of oxygen in the exhaust gases, making reduction reactions more difficult. There are commercial and environmental pressures encouraging lean-burn engines, because of their fuel economy. At the same time, however, there are technical pressures such as the difficulty in reduction of NOx already mentioned and the generally cooler exhaust gases caused by excess air in turn making it more difficult to reach temperatures over a catalytic convertor at which adequate conversion takes place.

The best-known approach for NOx conversion for lean-burn engines is applied commercially by the inclusion in the catalyst of a NOx storage component such as Ba, Ca *etc*, which operates to store NOx during lean operation. The NOx storage component releases absorbed NOx when the oxygen content of the exhaust gas is lowered. For example, EP 560991 describes such a system; lowering of the oxygen content of the exhaust gases is achieved by making the exhaust gases rich or stoichiometric by controlling the air-fuel ratio. Various techniques are available to achieve this, primarily involving designing the engine management system to provide rich "spikes" or excursions during normal lean running. It is our belief that all known practical examples of lean-burn engines incorporating such NOx storage concepts utilise either deliberate engine management strategies which provide $\lambda \geq 1$ excursions according to a predetermined assessment of the approach of saturation of the NOx storage component, or utilise the natural fluctuation of λ greater than 1 upon acceleration or some other part of the engine operating cycle.

In addition to the aforesaid EP 560991, other proposals to treat the exhaust gases from gasoline motors which operate at least predominately in the lean burn region, are

surfaces of the catalyst components) preferentially reacts with gaseous hydrocarbon and/or CO. Desirably, the catalyst components are designed to be deficient in oxygen and/or oxidising species compared to the exhaust gas, under normal running conditions.

NOx storage components suitable for use in the present invention include one or more alkali metal or alkaline earth metal compounds.

The present invention makes it possible to operate lean-burn engines of various types, especially direct-injection gasoline engines, constantly in the lean mode. This offers considerable promise in improved fuel consumption and may offer improvements in driveability. Additionally, the fundamentally different approach, relying on a catalyst designed to have the specified selectivity rather than on the storage of NOx, offers the skilled person greater opportunities for catalyst formulation than is the case with a conventional NOx storage catalyst. It will be readily appreciated that a catalyst that depends upon NOx storage will become saturated and will require periodic regeneration. In the present invention, for reasons that are not yet fully understood, NOx does not saturate the catalyst, although there may be, on the molecular level, storage of NOx as nitrate on the surface of certain of the catalyst components.

In accordance with the present invention, the catalyst is designed and formulated to achieve the desired selectivity. It is believed that, following the teaching of the present invention regarding the desirability of such selectivity, the skilled person can achieve such selectivity in a number of ways. A suitable catalyst is a supported catalyst with a platinum group metal and a NOx storage component together effective to catalyse the oxidation of NO to NO_2 and/or NO_3 in one layer and a second layer containing a platinum group metal effective to reduce NO to N_2. Preferably, the catalyst comprises a first layer comprising platinum and barium or calcium carried on a high surface area alumina-containing support. Preferably, the second layer of the catalyst comprises rhodium and cerium carried on a high surface area support which does not contain alumina. More preferably, there is no significant quantity of rhodium in the first layer, and no significant quantity of platinum or NOx storage component in the second layer.

variant. A yet further embodiment desirably uses low-sulphur fuel (*eg* less than 50ppm S) and low-sulphur lubricants, *eg* synthetic lubricants rather than those refined from crude oil, together with the novel catalytic convertor of the present invention.

The invention is illustrated with reference to the accompanying drawings, in which

Figure 1 is a chart showing emissions from a direct-injection engine fitted with a conventional NOx-trap catalyst, and

Figure 2 is a similar chart for the same engine fitted with a selective catalyst according to the invention.

A Mitsubishi Galant GDi was fitted with a conventional commercial high efficiency lean NOx Pt/Rh catalyst supported on an alumina washcoat carried on a 400 cells/ square inch cordeirite monolith. The catalyst formulation contains Ba which acts as a NOx store. The engine is controlled to run lean and at no time does the air/fuel ratio exceed $\lambda = 1$ during the ECE test cycle.

Referring to Figure 1, the speed is in the ECE cycle shown as a complex cycle, the accumulative NOx concentration is shown at two positions, before the catalyst ("engine out") and after the catalyst ("tailpipe"). It can be seen that engine out NOx accumulates steadily, whereas after about one minute the catalyst reaches operating temperature and begins to convert NOx to N_2. There is, however, a proportion of NOx which is not converted, so that the cumulative tailpipe emissions also increase constantly.

The same motor car was then fitted with an experimental catalyst whose preparation is described in detail below and the same tests performed. The results shown in Figure 2 show, after the initial period, a flat trace of cumulative tailpipe NOx emissions, indicating that all of the NOx emitted from the engine is being converted. Additional studies have shown that the expected NOx storage capacity has been exceeded many-fold. It is interpreted that the experimental catalyst shows unexpected and valuable selectivity for the reaction between NOx and/or nitrate with hydrocarbons and/or CO compared to the reaction between hydrocarbons and/or CO with oxygen. It is also interpreted that the novel catalyst

CLAIMS

1. A catalytic convertor for a lean-burn engine comprising a catalyst component capable of storing NOx, characterised in that the catalyst is constructed to incorporate a further catalyst component which exhibits greater selectivity for catalysing the reaction between NOx and/or nitrate with hydrocarbons and/or CO than for catalysing the reaction between hydrocarbons and/or CO with oxygen.

2. A catalytic convertor for a lean-burn engine, comprising a supported layered catalyst having a first layer containing a first platinum group metal and a NOx storage component together effective to catalyse the oxidation of NO to NO_2 and/or NO_3 and to store NO_3 as nitrate and further effective to release NO and O_2, and a second layer containing a second, different, platinum group metal, effective to reduce NO to N_2.

3. A catalytic convertor according to claim 2, wherein the first layer contains platinum and the second layer contains rhodium.

4. A catalytic convertor according to claim 3, wherein the first layer contains platinum carried on an alumina-containing washcoat and the NOx storage component is barium, and the second layer contains rhodium carried on a washcoat which does not contain alumina.

5. A catalytic convertor according to claim 4, wherein the first layer washcoat comprises alumina, ceria and zirconia, optionally as a mixed oxide of two or more thereof, and the second washcoat layer contains ceria and zirconia, optionally as a mixed oxide.

6. A catalytic convertor according to claim 3, wherein the first layer comprises platinum carried on an alumina washcoat which also incorporates potassium, and the second layer comprises rhodium carried on a ceria/zirconia washcoat and an interlayer comprising a washcoat and a barium compound is provided between said first and second layers.

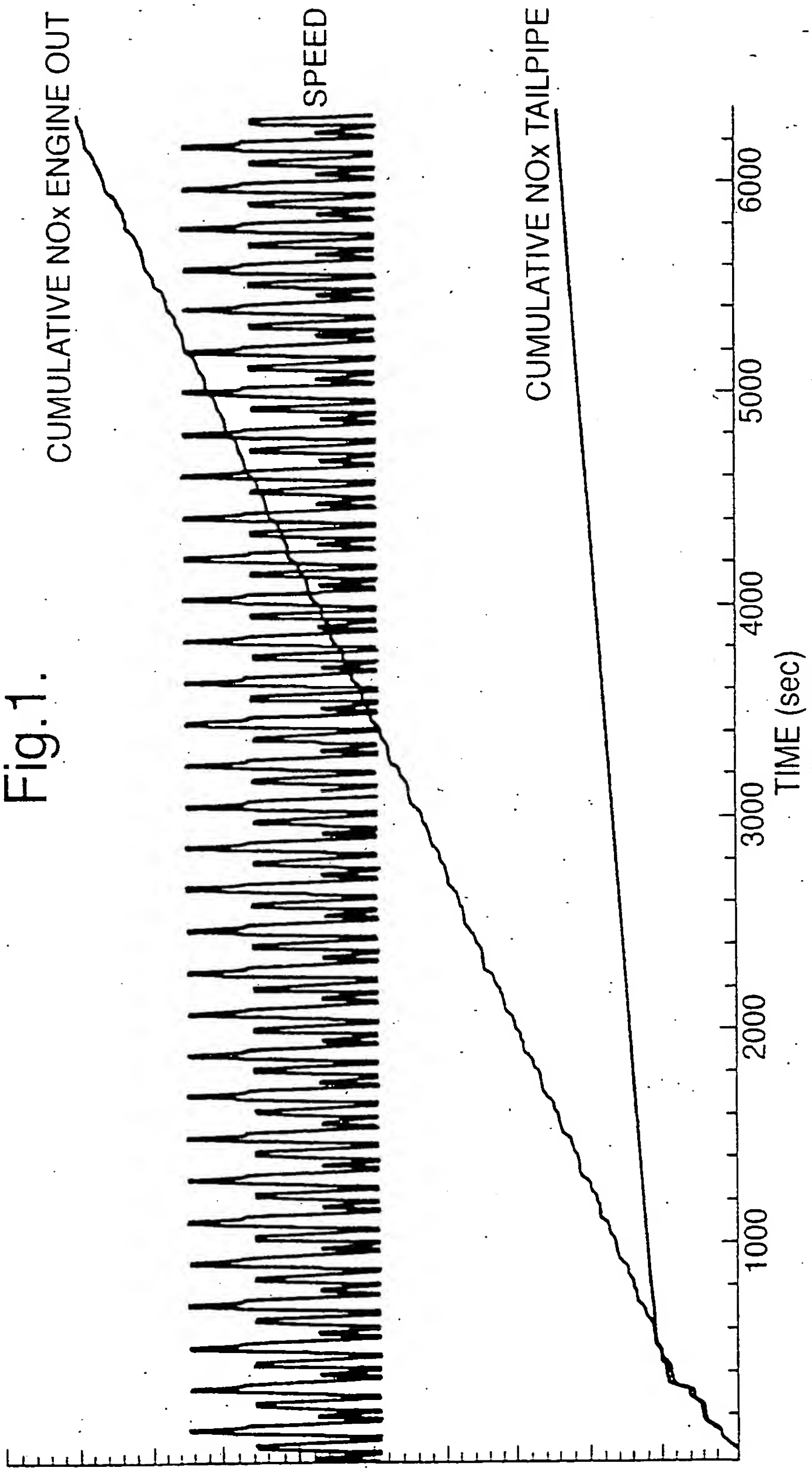
CUMULATIVE NOx ENGINE OUT
SPEED
CUMULATIVE NOx TAILPIPE
1000
2000
3000
4000
5000
6000
TIME (sec)

Fig.1.

INTERNATIONAL SEARCH REPORT

Interr. ial Application No
PCT/GB 98/01838

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 0 716 876 A (TOYOTA MOTOR CO LTD) 19 June 1996 cited in the application see page 2, line 54 - page 4, line 5 see page 4, line 16 - page 6, line 10 ---	1,2, 11-13 4,5,7,8
Y	US 5 459 119 A (ABE FUMIO ET AL) 17 October 1995 see column 2, line 38 - column 5, line 61 see column 8, line 25 - column 15, line 50; tables 1,2 ---	4,5,7,8
A	EP 0 669 157 A (TOYOTA MOTOR CO LTD ;CATALER IND CO (JP)) 30 August 1995 see page 4, line 50 - page 6, line 23; claims 1-22 --- -/--	1-5,7,8, 11,12

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 September 1998	07/10/1998

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INTERNATIONAL SEARCH REPORT

...formation on patent family members

Intern al Application No
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